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The dissociation energies of the alkaline earth oxides

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Our knowledge of the dissociation energies of the alkaline earth oxides is very poor. GAYDON (1) is only able to give rather uncertain data, determined by thermochemical and spectroscopic methods. One of us (A. L.) has in some papers (2, 3, 4, 5 and 6) carried out rotational and vibrational analyses of BeO, MgO, CaO, SrO and BaO. Everyone of these molecules possesses an unperturbed $^1\Sigma$-state as its lowest hitherto known state. The dissociation energies of these states have been determined by Birge-Sponer's method, which, however, gives very uncertain values here, owing to the long extrapolations. The thermochemical values, mentioned by Gaydon, also seem to be rather vague. One of us (L. H. (7)) has earlier used spectroscopical intensity measurements in flame spectra for thermochemical investigations, from which measurements it might be possible to determine dissociation energies of SrO and BaO. In this paper, we have collected the values of the dissociation energies for this group of oxides found with the above mentioned methods. Further, we have determined the values for MgO and CaO by experiments with the flame method.

The principle of this method is as follows. If a small amount of a metallic salt is inserted into the Lundegårdh acetylene-air flame, which gives a very stable emission, the salt becomes almost completely dissociated. The resulting state of thermochemical equilibrium depends only on the temperature and the composition of the flame. Assuming the oxidation

$$M + O \rightleftarrows MO$$

is the only reaction, in which an alkaline earth metal (M) takes part, the equation

$$\frac{p_M \cdot p_O}{p_{MO}} = K_{MO}\ (1), \tag{1}$$

determines the partial pressures p_M and p_{MO} of the metal atoms and the oxide.

For a diatomic molecule, Brigg's logarithm of the equilibrium function is

$$\log K_{MO}(T) = -5\,040 \frac{D_{MO}}{T} + \tfrac{3}{2} \log T - V_{MO}(T) + i_M + i_O - i_{MO}, \tag{2}$$

where

T = the absolute temperature,

D_{MO} = the dissociation energy in e.v.

i_M, i_O and i_{MO} are chemical constants for the corresponding constituents, and

$$V_{MO}(T) = \Sigma\, e^{-hc \cdot \frac{G(v)-G(0)}{kT}} \tag{3}$$

is the vibrational part of the distribution function. The pressures will be measured in atm:s.

The chemical constant for a monoatomic gas is calculated from the expression

$$i_M = -1.587 + \tfrac{3}{2}\log M + \log g_0 \qquad \begin{array}{l}(M = \text{atomic weight} \\ g_0 = \text{statistical weight of the} \\ \text{ground level})\end{array} \tag{4}$$

and for the (diatomic) oxide,

$$i_{MO} = -1.738 + \tfrac{3}{2}\log (MO) - \log B_e + \log g_0, \tag{5}$$

where MO = molecular weight, B_e = rotational constant (in cm^{-1}) and g_0 = the degree of degeneration of the ground level.

The above expressions are valid only if the populations of the upper electronic levels can be neglected.

In equ. (1), we now determine the partial pressure p_M by measuring the absolute intensity of an emitted spectrum line of the metal. $p_M + p_{MO}$ is calculated from the amount of the salt, injected into the flame per unit time. p_0 is computed from the temperature and the ratio acetylene : air, using the known thermochemical data (dissociation energies, etc.) for the common gases present in the flame. According to reference 7, the course of the experiment is:

1) Determination of the temperature of the flame by means of spectrum line reversal;

2) Measurement of the amounts of acetylene, air and aqueous solution (the latter is made to accompany the air by means of an atomizer), consumed per unit time,

3) Feeding the flame with a dilute solution of a salt (chloride) of the metal being investigated, and measuring the intensity of the resonance line of this metal relative to the intensity of a calibrated standard lamp at the same wave-length.

For determining the temperature, the flame was fed with a suitable solution of NaCl. The light from a tungsten band lamp was focussed on the flame (some mm above the top of the blue cone). The common image of the band and the flame was thrown on the slit of a spectroscope, and the current through the lamp adjusted until the yellow sodium doublet disappeared into the continuum. At this current intensity the black temperature of the band image was determined by means of an optical pyrometer. A correction was made for the difference between the wave-length of the Na line (5 890 Å) and the effective wave-length of the pyrometer (6 500 Å).

The flame-temperature was thus found to be 2 410° K.

The compositions of the constituents in the flame and the chemical equilibrium were determined in the way described on pages 58–59 of the reference 7. p_0 was found to be 2.2×10^{-4} atm.

The concentrations of the solutions used were 0.05–0.1 mol/liter $MgCl_2$ and 0.0005–0.001 mol/liter $CaCl_2$. For $BeCl_2$ no line was measurable. The measurements and the calculations of the absolute intensities and the pressures were made as described in reference 7. For the most concentrated solutions we obtained

$$p_{Mg} = 1.2 \times 10^{-6} \text{ atm.} \qquad p_{Ca} = 7.1 \times 10^{-8} \text{ atm.}$$

$$p_{MgO} = 8.2 \times 10^{-5} \text{ atm.} \qquad p_{CaO} = 8.3 \times 10^{-7} \text{ atm.}$$

From the values and equ. (1) and (2) the dissociation energies D_{MgO} and D_{CaO} were determined. In equ. (3), $G(v) = \omega_e (v + \frac{1}{2})$ should be inserted. On the assumption that MgO and CaO have the lower $^1\Sigma$-states found by one of us as the ground levels, the values of the constants ω_e and B_e (and $g_0 = 1$) determined in (3) and (4) should be substituted in equ. (3) and (5). On this assumption we have

$$D_{MgO} = 5.2 \text{ e.v.}, \qquad D_{CaO} = 5.2 \text{ e.v.}$$

The experimental accuracy of this method depends mainly on the temperature determinations and on the values used for the dissociation energies of the gas compounds in the flame. Assuming the error in the temperature determination to be as large as $\pm 40°$, the corresponding error in D is only about $\pm$ 0.1 e.v. The dissociation energies of the gas compounds are rather accurately known and the error in D due to these values must therefore be very small. The same is true of the other experimental data (composition of the flame, plate density measurements, etc.).

If the above-mentioned $^1\Sigma$-states are not the ground states, the values used of g_0, ω_e and B_e are incorrect. The influence on D of different ω_e- and B_e-values is of little importance. The value of g_0 is, however, six instead of one, if the ground state is a $^3\Pi$-term instead of a $^1\Sigma$-term. This corresponds to a decrease in D of about 0.4 e.v.

Table 1

The dissociation energies in e.v. of the alkaline earth oxides.

Molecule	Flame method	Thermo-chemical	Band spectroscopy	Dissociation products
BeO	—	—	3.9 − 2.0 = 1.9	Be (^{1}S) + O (^{1}D)
MgO	5.2	—	3.7 − 2.0 = 1.7	Mg (^{1}S) + O (^{1}D)
CaO	5.2	5.9	3.5 − 2.0 = 1.5 3.5 − 1.9 = 1.6	Ca (^{1}S) + O (^{1}D) Ca (^{3}P) + O (^{3}P)
SrO	4.8	4.5	3.3 − 2.0 = 1.3 3.3 − 1.8 = 1.5	Sr (^{1}S) + O (^{1}D) Sr (^{3}P) + O (^{3}P)
BaO	5.5	6.3	6.7 − 1.2 = 5.5	Ba (^{3}D) + O (^{3}P)

We would stress that in the calculations we have considered the metal as being present only as monoatomic vapour and oxide in the flame, and not as entering into other molecules (for instance Mg_2, MgN, MgC, MgH). This means that the values for the dissociation energies obtained are upper limits.

Table 1 gives the values of the dissociation energies from different methods. The second column contains the results with the method described here, the third column gives some thermochemical data (taken from Gaydon's book (1)), the fourth column contains the band spectroscopic results (Birge-Sponer extrapolation), diminished by the excitation energy of the dissociation products. In the fifth column we have given possible dissociation products.

The agreement between the data obtained from different methods is rather poor, except for BaO. This may be due to several factors. Thus it is very probable that some of the oxides (MgO, CaO and SrO) do not have the $^1\Sigma$-states as normal states. Another reason is that in some cases the Birge-Sponer's extrapolation gives very uncertain values. For SrO, for instance, only the vibrational levels 0 and 1 were analysed rotationally in the lower $^1\Sigma$-state.

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